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Structure of 2-[(4-Cyanophenyl)methylene]-1,3-dithiole-4,5-dicarboxylic Acid, Dimethyl Ester

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Abstract. $C_{15}H_{11}NO_4S_2$, $M_r = 333.39$, triclinic, $P\bar{1}$, $a = 20.611$ (7), $b = 9.452$ (5), $c = 7.856$ (4) Å, $\alpha = 98.52$ (3), $\beta = 96.05$ (2), $\gamma = 93.0$ (3)°, $V = 1502$ (2) Å^3, $Z = 4$, $D_x = 1.475$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 3.55$ cm^{-1}, $F(000) = 688$, $T = 293$ K, $R = 0.051$ ($wR = 0.059$) for 3388 reflections. The asymmetric unit contains two independent molecules which have a similar conformation. The dithiole ring is planar in both molecules and makes an angle with the phenyl ring of 2.1 and 0.6°, respectively. Thus the methylene-1,3-dithiole unit (electron donor) has a maximum π overlap with the phenyl ring, that bears a *p*-cyano group (electron acceptor). In both molecules the methyl esters are planar: one is almost parallel to the dithiole ring (angles of 9.8 and 8.5°, respectively) and the other makes angles of 54.2 and 63.8°, respectively.

Experimental. The title molecule (see scheme) was prepared following the procedure reported by Mulvaney & Chang (1980) for 2-(phenylmethylene)-1,3-dithiole-4,5-dicarboxylic acid, dimethyl ester, starting from *p*-cyanobenzaldehyde, dimethyl acetylenedicarboxylate and carbon disulfide in the presence of $(n\text{-Bu})_3$P in diethyl ether at 250 K. Orange–red cubes were obtained by recrystallization from acetonitrile, dimensions 0.4 × 0.5 × 0.5 mm.

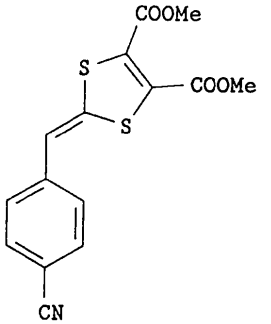

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Table 1. *Positional parameters and their estimated standard deviations*

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	B_{eq}*(Å^2)
S1	0.97420 (5)	0.2917 (1)	0.2758 (2)	4.31 (2)
C2	0.9848 (2)	0.1072 (4)	0.2607 (5)	3.18 (8)
S3	0.91830 (5)	0.0131 (1)	0.3257 (2)	3.90 (2)
C4	0.8708 (2)	0.1585 (4)	0.3641 (5)	3.51 (9)
C5	0.8958 (2)	0.2848 (4)	0.3362 (5)	3.82 (9)
C6	1.0393 (2)	0.0545 (4)	0.2074 (5)	3.47 (9)
C7	1.0587 (2)	−0.0919 (4)	0.1891 (5)	3.17 (8)
C8	1.0190 (2)	−0.2093 (4)	0.2160 (6)	4.9 (1)
C9	1.0410 (2)	−0.3443 (4)	0.1973 (7)	5.4 (1)
C10	1.1018 (2)	−0.3683 (4)	0.1480 (6)	4.1 (1)
C11	1.1421 (2)	−0.2550 (4)	0.1176 (6)	4.2 (1)
C12	1.1202 (2)	−0.1194 (4)	0.1395 (5)	3.63 (9)
C13	1.1220 (2)	−0.5133 (5)	0.1236 (7)	5.5 (1)
N14	1.1364 (2)	−0.6280 (4)	0.1038 (8)	8.3 (1)
C15	0.8618 (2)	0.4196 (5)	0.3430 (6)	4.9 (1)
O16	0.8083 (2)	0.4225 (4)	0.2631 (7)	11.0 (1)
O17	0.8913 (2)	0.5229 (3)	0.4351 (6)	8.2 (1)
C18	0.8613 (3)	0.6612 (5)	0.439 (1)	8.9 (2)
C19	0.8073 (2)	0.1314 (5)	0.4319 (6)	4.4 (1)
O20	0.7745 (2)	0.2241 (4)	0.4837 (5)	7.9 (1)
O21	0.7947 (1)	−0.0048 (3)	0.4358 (4)	5.63 (8)
C22	0.7371 (3)	−0.0462 (7)	0.5150 (7)	7.8 (2)
S31	0.55995 (6)	0.2155 (1)	0.2519 (2)	4.86 (3)
C32	0.5687 (2)	0.3954 (4)	0.2171 (5)	3.43 (9)
S33	0.49813 (5)	0.4862 (1)	0.2501 (1)	3.49 (2)
C34	0.4519 (2)	0.3425 (4)	0.3053 (5)	3.08 (8)
C35	0.4807 (2)	0.2197 (4)	0.3049 (5)	3.37 (8)
C36	0.6250 (2)	0.4476 (4)	0.1714 (5)	3.72 (9)
C37	0.6425 (2)	0.5919 (4)	0.1383 (5)	3.36 (9)
C38	0.6024 (2)	0.7047 (4)	0.1500 (6)	4.3 (1)
C39	0.6221 (2)	0.8373 (4)	0.1133 (6)	4.4 (1)
C40	0.6831 (2)	0.8617 (4)	0.0663 (5)	3.79 (9)
C41	0.7241 (2)	0.7518 (5)	0.0540 (6)	4.9 (1)
C42	0.7045 (2)	0.6205 (5)	0.0911 (6)	4.3 (1)
C43	0.7033 (2)	1.0000 (5)	0.0292 (6)	4.9 (1)
N44	0.7193 (2)	1.1109 (5)	0.0011 (6)	7.1 (1)
C45	0.4501 (2)	0.0845 (4)	0.3537 (5)	3.61 (9)
O46	0.4359 (2)	0.0727 (3)	0.4927 (4)	4.85 (7)
O47	0.4453 (2)	−0.0199 (3)	0.2194 (4)	4.67 (7)
C48	0.4192 (3)	−0.1591 (5)	0.2490 (7)	5.7 (1)
C49	0.3841 (2)	0.3644 (4)	0.3392 (5)	3.65 (9)
O50	0.3451 (1)	0.2732 (3)	0.3564 (4)	5.46 (8)
O51	0.3731 (1)	0.5018 (3)	0.3447 (4)	4.87 (7)
C52	0.3077 (2)	0.5411 (6)	0.3740 (8)	6.8 (1)

The cell parameters were obtained by least-squares fit using 25 centered reflections with $6 < \theta < 25°$. An Enraf–Nonius CAD-4 diffractometer was used for data collection, 5292 unique reflections, $-24 \le h \le 24$, $-11 \le k \le 11$, $0 \le l \le 9$, $[(\sin\theta)/\lambda]_{max} = 0.5947$ Å^{-1}. Intensities were measured in the $\omega/2\theta$

Table 2. *Bond distances* (Å) *and angles* (°)

Numbers in parentheses are estimated standard deviations in the least significant digits.

S1—C2	1.757 (4)	S31—C32	1.765 (4)
S1—C5	1.733 (4)	S31—C35	1.730 (4)
C2—S3	1.757 (5)	C32—S33	1.750 (5)
C2—C6	1.334 (6)	C32—C36	1.342 (6)
S3—C4	1.737 (4)	S33—C34	1.752 (4)
C4—C5	1.332 (6)	C34—C35	1.330 (5)
C4—C19	1.490 (7)	C34—C49	1.469 (6)
C5—C15	1.482 (7)	C35—C45	1.512 (6)
C6—C7	1.452 (5)	C36—C37	1.460 (6)
C7—C8	1.399 (6)	C37—C38	1.381 (6)
C7—C12	1.390 (6)	C37—C42	1.392 (6)
C8—C9	1.369 (6)	C38—C39	1.377 (6)
C9—C10	1.371 (6)	C39—C40	1.365 (6)
C10—C11	1.385 (6)	C40—C41	1.373 (6)
C10—C13	1.445 (7)	C40—C43	1.431 (6)
C11—C12	1.375 (6)	C41—C42	1.366 (7)
C13—N14	1.132 (6)	C43—N44	1.142 (7)
C15—O16	1.214 (6)	C45—O46	1.180 (5)
C15—O17	1.218 (5)	C45—O47	1.326 (4)
O17—C18	1.473 (6)	O47—C48	1.456 (5)
C19—O20	1.186 (6)	C49—O50	1.181 (6)
C19—O21	1.305 (6)	C49—O51	1.326 (5)
O21—C22	1.458 (7)	O51—C52	1.449 (6)

C2—S1—C5	96.7 (2)	C32—S31—C35	96.6 (2)
S1—C2—S3	112.1 (2)	S31—C32—S33	112.3 (2)
S1—C2—C6	120.2 (4)	S31—C32—C36	120.1 (4)
S3—C2—C6	127.6 (3)	S33—C32—C36	127.6 (4)
C2—S3—C4	96.8 (2)	C32—S33—C34	96.7 (2)
S3—C4—C5	117.0 (3)	S33—C34—C35	116.6 (3)
S3—C4—C19	116.9 (3)	S33—C34—C49	117.9 (3)
C5—C4—C19	126.1 (4)	C35—C34—C49	125.4 (4)
S1—C5—C4	117.3 (3)	S31—C35—C34	117.7 (4)
S1—C5—C15	116.2 (4)	S31—C35—C45	117.3 (3)
C4—C5—C15	126.4 (4)	C34—C35—C45	124.9 (4)
C2—C6—C7	129.5 (4)	C32—C36—C37	129.0 (4)
C6—C7—C8	124.1 (4)	C36—C37—C38	125.3 (4)
C6—C7—C12	118.8 (3)	C36—C37—C42	118.4 (4)
C8—C7—C12	117.1 (4)	C38—C37—C42	116.3 (4)
C7—C8—C9	120.7 (4)	C37—C38—C39	121.9 (4)
C8—C9—C10	120.9 (5)	C38—C39—C40	120.3 (4)
C9—C10—C11	119.9 (4)	C39—C40—C41	119.0 (4)
C9—C10—C13	119.0 (4)	C39—C40—C43	120.0 (4)
C11—C10—C13	121.1 (4)	C41—C40—C43	120.9 (5)
C10—C11—C12	118.9 (4)	C40—C41—C42	120.4 (5)
C7—C12—C11	122.4 (4)	C37—C42—C41	121.9 (4)
C10—C13—N14	178.5 (5)	C40—C43—N44	179.5 (6)
C5—C15—O16	121.0 (4)	C35—C45—O46	124.9 (3)
C5—C15—O17	114.8 (4)	C35—C45—O47	109.5 (3)
O16—C15—O17	124.2 (5)	O46—C45—O47	125.5 (4)
C15—O17—C18	116.9 (4)	C45—O47—C48	115.9 (3)
C4—C19—O20	123.4 (4)	C34—C49—O50	125.2 (4)
C4—C19—O21	111.6 (4)	C34—C49—O51	109.7 (3)
O20—C19—O21	125.1 (4)	O50—C49—O51	125.1 (4)
C19—O21—C22	117.8 (4)	C49—O51—C52	116.6 (3)

scan mode [scan speed 4.1° s^{-1}, scan width (θ) 1 + 0.34tanθ°]. Decay of three control reflections, measured every hour, was < 1%. Correction was made for Lorentz and polarization factors. Number of observed reflections 3388 [$F_o^2 > 3\sigma(F_o^2)$]. No absorption correction was used.

Structure solved by direct methods (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares. Weights for each reflection in the refinement (on F) were calculated from $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$; the value of the instability factor p was determined as 0.04. H atoms were placed in calculated positions and were refined. The number of parameters refined was 486: scale factor, isotropic extinction factor g [$F_{corr} = F_c/(1 + gI_c)$; final value 2.1×10^{-7}], positional and anisotropic thermal parameters for non-H atoms and positional and isotropic thermal parameters for H atoms.

Refinement converged at $R = 0.051$, $wR = 0.059$, $S = 1.88$, $(\Delta/\sigma)_{max} = 0.2$. Largest peak on the final difference Fourier map 0.40 e $Å^{-3}$. All calculations were performed using *SDP* (Frenz & Associates, Inc., 1983). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic parameters of non-H atoms are given in Table 1.* Bond distances and bond angles are given in Table 2. Atom numbering of the title compound is shown in Fig. 1.

Related literature. To the best of our knowledge no crystal structure of a *para*-substituted aromatic ring with a 4,5-functionalized methylene-1,3-dithiole moiety as electron donor and a cyano group as electron acceptor has been published. However, some related structures have been determined. The crystal structure of a dithiinofulvene derivative with a methylene-1,3-dithiole-4,5-dicarboxylic

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete lists of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54552 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0486]

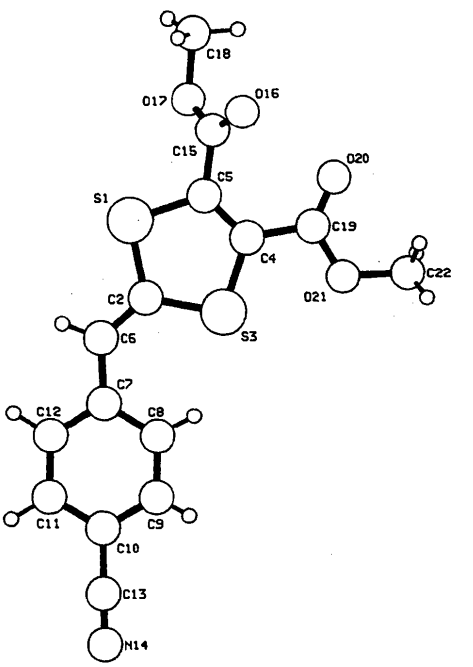

Fig. 1. View of one independent molecule with the atom-numbering scheme. The atom numbers in molecule (2) are obtained by adding 30 to those of molecule (1).

acid, dimethyl ester unit has been reported by Lakshmikantham, Cava & Carroll (1984). A niobium complex with a methylene-1,3-dithiole-4,5-bis-(trifluoromethyl) unit has been published by Amaudrut, Sala-Pala, Guerchais & Mercier (1990). Beer, Frew, Johnson & Paul (1970) have reported an isothiathiophten containing a methylene-1,3-dithiole-4-(4-bromophenyl) unit. The structure of (pivaloylmethylene)-1,3-dithiole-4-pivaloyl has been reported by Galloy, Declercq & Van Meerssche (1978). A 4,5-unsubstituted methylene-1,3-dithiole derivative has been reported by Barnes, Paton & Nicholls (1982). The structures of the related compounds mentioned here are less accurate than that reported in this paper.

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Structure of Methyl 2-(2,5-Dihydro-2-oxo-3-phenyl-5-furyl)lactate

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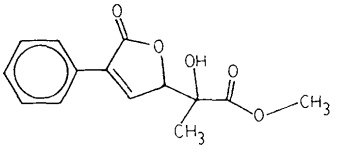
Abstract. $C_{14}H_{14}O_5$, $M_r = 262.26$, monoclinic, $P2_1/n$, $a = 11.319$ (3), $b = 6.5115$ (15), $c = 18.105$ (5) Å, $\beta = 105.660$ (20)°, $V = 1284.8$ (6) Å^3, $Z = 4$, $D_x = 1.356$ g cm^{-3}, λ(Cu $K\alpha_1$) = 1.54056 Å, $\mu = 8.26$ cm^{-1}, $F(000) = 553.89$, $T = 295$ K, $R = 0.036$, $wR = 0.033$ for 1692 reflections with $I > 2.5\sigma(I)$. The structure determination established the identity of the product of a $Co_2(CO)_8$-catalyzed carbonylation reaction with an epoxy alcohol.

Experimental. A colourless crystal of the title compound (1) was grown from THF solution. Cell parameters from 20 reflections in the 2θ range 85–90°. Data were collected on a Picker diffractometer using profile analysis (Grant & Gabe, 1978). Three standards measured every 100 reflections were used for scaling and had an overall drop in intensity of 6%. Averaging of symmetry-equivalent reflections gave a merging R value of 3.3%. Parameters related to crystal data and intensity collection are given in Table 1. The structure was solved by direct methods and refined by cycles of least-squares calculations. H atoms were located in a difference map and refined isotropically. Final atomic parameters are listed in Table 2. All non-H atoms were refined anisotropically. All computing was performed with the *NRCVAX* system of structure-solving programs (Gabe, Le Page, Charland, Lee & White, 1989). Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).*



(1)

An *ORTEP*II plot of (1) is shown in Fig. 1. Bond lengths and angles, except those involving H atoms, are given in Table 3. A stereoplot showing packing of the unit cell has been included as Fig. 2. The structure consists of a planar lactone ring with maximum deviation from planarity 0.0098 (18) Å, rotated slightly from the plane of the phenyl ring, with a dihedral angle of 16.73 (6)°. The diastereomer adopts an *anti* configuration. The molecules are packed with the lactone rings approximately parallel to the b axis. The closest intermolecular approach is 2.14 (2) Å

* Lists of structure factors, anisotropic thermal parameters and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54457 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0352]

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